Electrical Resistance of Thin Films Deposited by Kathode Discharge.

By

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A Thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[Reprinted from the Physical Review, Vol. XI., Nos. 1 and 2, July–August, 1900.]

PRESS OF
THE NEW ERA PRINTING COMPANY,
LANCASTER, PA.

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

EDWARD L. NICHOLS
ERNEST MERRITT, AND FREDERICK BEDELL

Two volumes of THE PHYSICAL REVIEW are published annually, these volumes beginning in July and January, respectively, and containing at least five numbers each. The price of subscription is two dollars and fifty cents a volume (five dollars a year), or fifty cents a number. Subscriptions should be sent to the publishers. THE MACMILLAN COMPANY, 41 *North Queen Street, Lancaster, Pa.*, or 66 *Fifth Avenue, New York;* Messrs. MACMILLAN & CO., LTD., *London;* or to Messrs. MAYER AND MUELLER, *Berlin.*

Previous to Volume V. (July–December, 1897) THE PHYSICAL REVIEW was published in annual volumes, each containing six bimonthly numbers, beginning with the July–August number, 1893. These may be obtained from the publishers at the former subscription price, three dollars per volume.

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PUBLISHED FOR CORNELL UNIVERSITY

THE MACMILLAN COMPANY

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ELECTRICAL RESISTANCE OF THIN FILMS DEPOSITED BY KATHODE DISCHARGE.

BY A C LONGDEN.

INTRODUCTION.

IF standard high resistances of great precision and unvarying values could be obtained at low cost, their application in the determination of insulation resistance by the direct deflection method would soon cease to be their sole field of general usefulness. The condenser and ballistic galvanometer would no longer be regarded as important or even desirable in comparing electromotive forces, and a high resistance could even be used with some advantage in place of a condenser, in the condenser method, for measuring internal battery resistance.

The use of numerous shunts in the determination of figure of merit is always regarded as something to be endured rather than desired. With a suitable high resistance in series with the galvanometer and standard cell, the determination of figure of merit becomes absolutely simple. The range of the Wheatstone bridge may also be enormously increased by the use of high resistances as bridge arms, and heavy currents may be measured with delicate galvanometers in series with high resistances, without making the resistance of the shunt through which the main current passes so small that the percentage of error in the calculations shall be large.

The use of carbon as a high resistance material is tolerably satisfactory for some purposes, if we are willing to re-standardize our resistances every time we use them, and to reckon with the enormously high temperature coefficient of the material; even then, the uncertainty of the contacts in most forms of carbon resistances is so great as to condemn such resistances in all cases where anything like careful or accurate work is contemplated.

A number of forms of carbon resistances have been used in connection with the research which furnishes the subject matter of this

article. It would not be in place to give detailed descriptions of them here, but it may be well to say in passing, that those which were the most nearly trustworthy consisted of sticks of pipe clay saturated with sugar solutions, of different degrees of concentration —the sugar being subsequently carbonized in the sticks by continued exposure to a red heat, in the absence of oxygen. The resistance of the stick depends upon the degree of concentration of the sugar solution used in preparing it.

While these resistances were very satisfactory for carbon, it must still be said that no carbon resistance can be considered for a moment in comparison with standard wire resistances.

In wire resistances, the use of alloys instead of pure metals is based upon the fact that alloys have, in general, lower temperature coefficients and higher specific resistance than pure metals ; but it must be borne in mind that, so far as high specific resistance is concerned, it is not in itself an advantage, but is only a means to an end. A wire, having a high specific resistance, enables us to obtain a high resistance, having small weight, small bulk and comparatively low cost. If these conditions could be met as well or better in some other way, high specific resistance would be of no importance whatever.

Alloys are certainly inferior to pure metals in some respects. Aside from the molecular rearrangement which may be going on in either the alloy or pure metal, alloys suffer from disintegration and possibly from internal chemical changes which are impossible in pure metals. It is also true that alloys frequently suffer from contact with their surroundings. Manganin, for example, is very easily oxidized, and is even pronounced by some investigators as worthless. Among the pure metals there are several which resist oxidation and other chemical changes admirably. Now if it is possible to obtain a high resistance in the form of a pure metal, and at the same time to retain all the advantages of an alloy, such a resistance ought to soon find favor in the electrical world.

From the results of some work done a few years since by Miss Isabelle Stone,[1] we have reason to believe that metals in the form of

[1] "On the Electrical Resistance of Thin Films," Physical Review, Vol. 6, pp. 1–16.

thin films upon glass exhibit certain qualities unlike those of the same metals in the ordinary form. Miss Stone reached three conclusions, which may be stated as follows :

1. The electrical resistance of such films as she investigated decreases in value quite rapidly for a short time, then less rapidly for a much longer time.

2. The higher the resistance of the film, the more rapid is the decrease in value.

3. For very thin films, the ratio of the measured resistance to the calculated resistance is high.

Miss Stone's research included silver films only, and these were deposited from aqueous solutions by what is known as the Rochelle salt method ; but her work is suggestive of a very large field of research, if other methods of deposition could be used.

As early as 1877 Professor A. W. Wright[1] of Yale, described a method of depositing thin metallic films upon glass by electrical discharge. Professor Wright produced both opaque and transparent mirrors from a large number of metals, pointed out the difference in rate of deposition of different metals, and suggested that on account of the difficulty of depositing aluminum and magnesium, these metals should be used for electrodes in vacuum tubes in order to avoid the discoloration so common in the neighborhood of the kathode when platinum electrodes are employed.

About two and a half years ago it was my good fortune to learn the practical details of Professor Wright's process in Ryerson Physical Laboratory at the University of Chicago ; and to have the opportunity of preparing a number of mirrors and thin metallic films, with the admirable apparatus designed for this purpose by Professor Stratton and Dr. Mann, of that institution.

Deposition of Films.

The deposition is effected in a vacuum, by a process which may here be included for convenience under the general term kathode

1 "On the Production of Transparent Metallic Films by the Electrical Discharge in Exhausted Tubes," Am. Journal of Science and Arts, Vol. 13, pp. 49–55.

"On a New Process for the Electrical Deposition of Metals and for Constructing Metal-Covered Glass Specula," Am. Journal of Science and Arts, Vol. 14, pp. 169–178.

discharge,[1] from an electrode consisting of the metal to be deposited.

The necessary apparatus for doing the work advantageously includes a vacuum pump capable of reducing the pressure in the receiver to a few millionths of an atmosphere; an induction coil capable of producing a spark eight or ten centimeters long; an interrupter making a complete break in the circuit, and preferably of high frequency; and a source of electrical energy, capable of furnishing a current of several ampères, at a pressure of not less than fifty volts, if the Wehnelt interrupter is used.

The pump used in the part of the work done in Chicago was a double acting Geissler pump, all glass, and exhausting into a very good secondary vacuum at each end of the stroke, so that the mercury in the main pump was never in contact with the air. This pump is capable of producing a splendid vacuum, but must be rather carefully handled, as the tendency to develop leaks is somewhat aggravated by the fact that the entire apparatus is in continual motion when in use.

In continuing the work at Columbia University, it seemed desirable to construct a pump which should be free from constant danger of developing leaks, and which should be capable of producing the required vacuum rapidly and easily. The Sprengel pump is slow, and the ordinary Geissler pump with its numerous ground joints, valves and stop-cocks, and its rubber connecting tube, is a little uncertain, and at best, somewhat less effective than the necessities of this case require. A Geissler pump was finally decided upon, but not without a determination to eliminate some of its objectionable features.

Figure 1 shows a diagram of the working parts. The right-hand side of the pump, as viewed in the diagram, is in some respects similar to the Bessel-Hagen[2] pump, but simpler. The tube (*A*) leading from the exhaust chamber to the receiver rises to the height of a full meter above the level of the mercury at (*B*), when the reservoir (*C*) is elevated. This feature of the apparatus is used instead

[1] The nature of the process will be considered more in detail hereafter.

[2] "Ueber eine Neue Form der Toepler'schen Quecksilberluftpumpe und einige mit ihr angestellte Versuche," Wied. Ann., Vol. 12, pp. 425–445.

of a valve to prevent the flow of mercury from the exhaust chamber (D) to the receiver. As the mercury sometimes rises in this tube with considerable momentum, it reaches a point considerably above barometric height, but the bulb (E), two or three centimeters in diameter, arrests any unusually active mercury which might otherwise pass around the bend at the top of the tube. The tube (F) completes the passage to the receiver, by way of the drying chamber (G), which is sealed on with the blow-pipe. There are no ground joints or even mercury seals in any part of the apparatus.

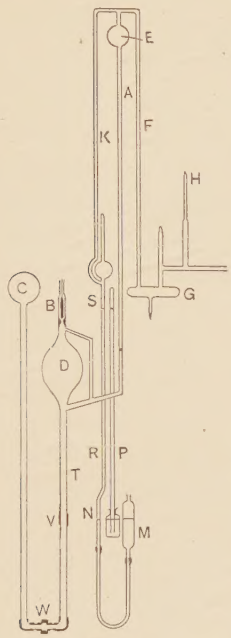

Fig. 1.

The tube (H) is a capillary through which air may be gradually admitted when the receiver is to be opened. The tube (K) leads to the McLeod gauge (L). The reservoir (M) is for the purpose of filling the McLeod gauge. Before beginning to exhaust, the mercury in the gauge tube stands at (N), at the same level as the mercury in the cistern of an independent barometer (P). As the exhaustion proceeds the mercury rises in the tube (R) until it stands at (S), the level of the mercury in the independent barometer. Of course the tube (R) answers the purpose of a gauge until the mercury rises so high that the difference between the two mercury columns is not easily readable. After this the McLeod gauge is used.

The rubber tube which usually connects the reservoir with the exhaust chamber in the Geissler pump is entirely displaced in this case, by an iron pipe with a swinging joint. This improvement originated with Professor Wm. Hallock, of Columbia. The glass tube (T) extends downward from the exhaust chamber as far as (V), where it is securely cemented into an enlargement on the iron pipe. From this point on to the reservoir (C) the mercury passage consists entirely of iron pipe. The swinging joint (W) is a carefully selected pipe union with well polished bearing surfaces moving upon a leather washer. The reservoir is raised and lowered by

simply swinging the pipe, and the rubber tube is thus entirely eliminated.

This pump has now been in use several months, and its behavior is most thoroughly satisfactory. Entire freedom from danger of leaks is a source of inestimable satisfaction in work of this kind. The results obtained are so uniform that, as long as the same receiver is used, it is easy to tell before beginning an operation, just how many strokes will be necessary to produce a certain degree of attenuation in the receiver. So confidently can this uniformity of results be relied upon that the McLeod gauge has become almost unnecessary.

The exact degree of exhaustion which this pump is capable of producing has not been carefully determined, because it has not been necessary to push it to its limit; but the fact that a pressure of one hundred thousandth of an atmosphere may be reached with extreme ease and certainty is evidence that the limit of usefulness of the pump has not been approached.

Notwithstanding the fact that this pump is single-acting and open to the air at one end of the stroke, the necessary vacuum for the deposition of metals can be produced with it in less than half the time required for the same operation with the double-acting pump already referred to.

The induction coil used in the earlier experiments was a large one, capable of producing a 30-cm. spark in air. The coil used later was not more than half as large; but a coil half the size of either of them would be abundantly large for the purpose.

The current interrupter used in the early part of the work was a mechanical interrupter operated by an electric motor in a separate circuit. The speed of the motor was usually about 1,500 revolutions per minute, with two breaks per revolution. This was quite satisfactory except that the deposition of metal would have been more rapid with an interrupter of greater frequency. The Wehnelt interrupter[1] is so well suited to this work that no other has been used since its advent.

The receiver in which the films are deposited is represented in vertical section in figure 2. (*AA*), figure 2, is a rubber stopper through which a glass tube (*B*) enters the receiver. This tube serves at

[1] Elektrotechnische Zeitschrift, Vol. 20, pp. 76–78.

once as an exhaust tube and as a passage way for the kathode wire (*C*). The tube and stopper are securely cemented into the open top of the receiver, with sealing wax (*DDDD*). The lower end of the kathode wire terminates in a thin aluminum tube, just large enough to drive firmly into the lower end of the glass tube (*B*). The kathode plate (*E*) which consists of the metal to be deposited, is supported by an aluminum rod (*F*), which slides into the thin aluminum tube with just enough friction to hold it in place. (*G*) is a heavy aluminum base plate, which serves as the anode, and (*H*) is an additional aluminum plate, which serves as a support for the glass plate (*L*), upon the upper surface of which the film is to be deposited. The dimensions may be taken from the figure as it is drawn to scale.

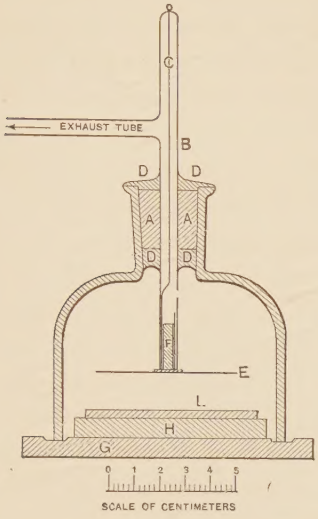

Fig. 2.

When the air is exhausted from the receiver and discharges from the kathode of an induction coil take place from the surface of (*E*), particles of the kathode plate (*E*) are deposited in the form of a brilliant film upon the surface of the glass plate (*L*) and, in fact upon the entire inner surface of the receiver.

The character of the film depends largely upon the rate of deposition, and this in turn depends upon the vacuum, the electromotive force, the current, the frequency of the interrupter and the distance from the kathode to the glass plate upon which the film is to be deposited. If all the conditions are properly adjusted, moderately rapid deposition will produce films of great hardness, density and brilliancy. If the deposition is too rapid, the resulting films will possess these qualities in less degree.

The factors which have been enumerated as affecting the rate of deposition are so intimately related, and so dependent upon each other, that it is quite impossible to discuss them independently. Professor Wright produced beautiful mirrors from a very small

kathode in a 2 mm. vacuum at a 3 mm. distance with a primary electro-motive force of perhaps a dozen volts, but in order to obtain an even distribution of metal over any very considerable surface, he found it necessary to keep the kathode moving over the surface during the process of deposition. It is just as easy to obtain an even distribution of metal over a large surface from a stationary kathode by using a correspondingly large kathode and placing it at a large distance from the glass. This, however, involves working in a higher vacuum and using a higher electro-motive force; and in order that the process may be as rapid, it necessitates using either a stronger current or a higher interruption frequency. A glass surface 5×6 centimeters may be beautifully platinized by placing it at a distance of 12 or 15 millimeters from a kathode plate of similar dimensions, in a vacuum of from .0001 to .00001 of an atmosphere, and operating with a primary current of 5 or 6 ampères at 110 volts, and with an interrupter frequency of about 300 per second.

The two factors, vacuum and distance, are related to each other in a way which demands a more detailed consideration. With a certain fixed vacuum, if the distance from the kathode to the glass plate is much too great, the film will be soft and spongy; while if

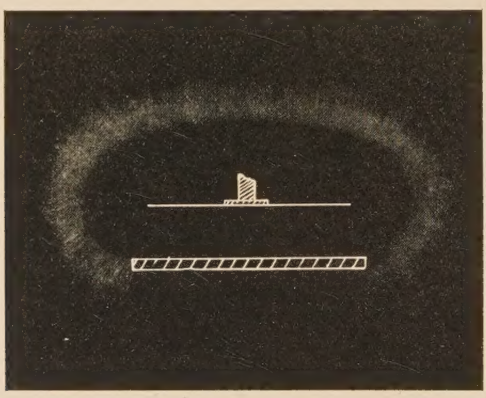

Fig. 3.

the distance is much too small it is almost impossible to get any metal deposited at all. It is found by experiment that the golden mean between these two extreme conditions is attained when the surface of the glass plate is just about in the plane which marks the

boundary between the kathode space and the luminous glow which surrounds it. (See figure 3.) Films deposited at other positions vary very greatly in hardness and density. Some platinum films will scarcely endure the touch of a camel's hair brush, while others can scarcely be removed from the glass by the most vigorous rubbing, or by the action of hot aqua regia.

At the suggestion of Professor Rood an attempt was made to discover the condition of the metal during its transition through the kathode space. A glass plate 5 × 6 centimeters, was placed at the usual distance, about 15 mm. from the kathode. In the center of this plate was placed a small aluminum stand, supporting a small glass plate about 12 millimeters square, within 3 mm. of the kath-

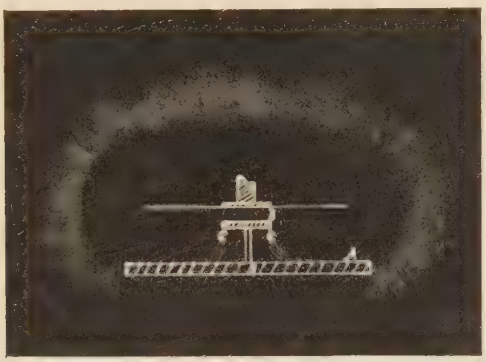

Fig. 4.

ode, as in Fig. 4. The air was then removed from the receiver until the kathode space just reached the surface of the large glass plate (*A*). A platinum film of considerable thickness was then deposited. When the plates were removed from the receiver, it was found, first that the film on the upper surface of the small plate (*B*) was exceedingly thin; next, that the stand had not cast a distinct shadow, but that the film on the large plate under the stand gradually shaded off to a comparatively thin center, as if the particles of platinum had drifted under the stand in considerable quantities. The third and most surprising fact to be noted was that the unprotected corners of the small plate were quite heavily coated on the *under* side.

In the light of these facts there can scarcely be any doubt in regard to the nature of the process. The surface of the kathode is

intensely heated, and particles, probably molecules, possibly smaller particles,[1] are projected into space. These particles radiate from the kathode in the gaseous form until they reach the limit of what is called the kathode space. In other words the kathode space *is* the space in which the metallic matter radiated from the kathode is still in the gaseous state. When the temperature has fallen to a sufficient degree, condensation begins, and we have the visible glow just outside the kathode space—a miniature snow-storm.

The very hot metallic gas near the kathode will not easily adhere to and condense upon the glass, and the comparatively cool "*vapor*," if we may use the term, condenses in rather a loose, soft, spongy layer. It is on this account that the best mirrors are formed just in the *edge* of the kathode space, as described on page 47.

This view is supported by the fact that the visible glow rises to the edge of the small stand as represented at (*C*), in figure 4. The metallic gas flowing over the surface of the stand is cooled somewhat, and the snow-storm therefore begins at a shorter distance from the kathode in this region than in the free space in the other parts of the receiver. Further evidence is offered in the fact that the glow around the stand is more conspicuous at first than it is after the stand itself has become somewhat heated.

The process seems to be simple distillation, in which the vaporization of the kathode depends *largely* upon its electrification.[2] That the process is not *entirely* dependent upon electrification, however, is evident from the fact that selenium, which *boils* at about 700 degrees, is deposited thousands of times more rapidly than platinum.

It is a noteworthy fact that when a rectangular kathode is used in a cylindrical receiver, the deposit on the sides of the receiver is thickest at small areas opposite the corners of the kathode. This is not because the distance is less, but because the surface density of the charge is greater at these points.

[1] J. J. Thompson, in Phil. Mag., Dec., 1899, "On the Masses of the Ions in Gases at Low Pressures," says that in case of the stream of negative electrification which constitutes the kathode rays, there are reasons for thinking that the charge on the ion is not greatly different from the electrolytic one, and that in the former case we have to deal with masses *smaller than the atom*.

[2] See Sir WilliamCrookes "On Electrical Evaporation," Electrical Review, Vol. 28, pp. 796–798 and 827, 828.

In conducting this process, it is not an easy matter to keep the vacuum at a fixed value during the first part of the experiment. When the circuit is first closed, the effect is to drive off the residual air and occluded gases. This produces a change of pressure in the receiver, which is quite rapid at first, but less and less rapid as the process continues. The rate at which the first change takes place depends largely upon the nature of the kathode, the condition of the atmosphere to which it has been exposed and the length of the exposure.

Under what might be called ordinary conditions, when a platinum kathode is used, it is not well to allow the current to continue more than a few seconds when first turned on, without stopping to observe the condition of the vacuum. If the vacuum is allowed to fall below .0001 of an atmosphere[1] there is danger of the film being rather soft. The film in this condition will not adhere well to the glass. Hence the importance of being particularly careful about the vacuum at first.

The curves (*A*) (*B*) and (*C*) in figure 5, represent the rate of deterioration of the vacuum during the rapid part of its change. The vertical portions of the curves represent intervals during which the coil is not in operation, but the pump is being used to improve the vacuum. These curves are all three for platinum films. Curve (*A*) represents an extreme case in which, after depositing a film, the receiver had been quickly opened, the film removed, new glass inserted and the receiver again sealed and exhausted—all within a few minutes. Curve (*C*) represents another extreme case in which both the kathode and the inside of the receiver had been exposed to the air for a long time and under very unfavorable conditions. Curve (*B*) may be said to fairly represent the deterioration of the vacuum during the first ten minutes of the process under average conditions. It must be understood that in all these cases, the minutes represented on the axis of abscissæ are not consecutive minutes, but minutes during which the process of deposition is actually going on.

Usually after ten or fifteen minutes of *actual deposition*, the condition of the vacuum does not change much and the deposition

[1] With the distance, voltage, etc., as stated on page 47.

may then go on continuously if the strength of the current used is not such as to heat the receiver excessively. After this stage has been reached, if the process is discontinued for half an hour or so, if there has been no perceptible leakage, the vacuum is found to

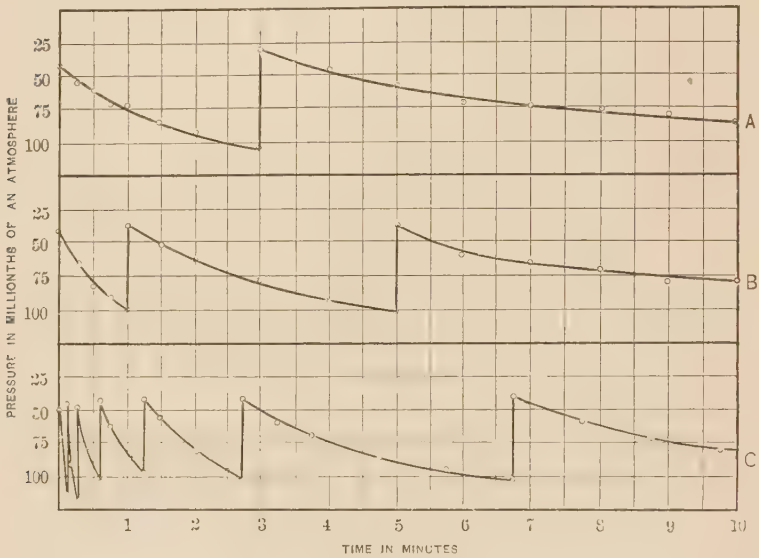

Fig. 5.

have improved considerably on account of the fact that most of the residual gas in the receiver has been occluded by the kathode and film. If the current be again started, however, the vacuum will soon fall to about its normal value.

Electrical Properties of Films.

Besides possessing splendid reflecting surfaces, such as commend them strongly for all high grade optical work, and besides displaying the colors of the different metals by transmitted light, and the selective absorption of different thicknesses of the same film, metallic films deposited in accordance with the method here described possess certain advantages as electrical resistances.

Without an exact method of determining the thickness of a film it is impossible to make an exact estimate of its specific resistance; but even with only an approximate determination of thickness, the

very rapid increase in resistance corresponding to diminishing thickness is so conspicuous as to leave no room for doubt that in *thin* films the ratio of the measured resistance to the calculated resistance is high. For example, a platinum film 5 cm. long, 15 mm. wide and .0002 mm. thick has a resistance of only a few ohms, while a film apparently about one tenth as thick [1] has a resistance of several hundred ohms, and a film probably about one hundredth as thick, has a resistance of hundreds of thousands or even millions of ohms.

There is plenty of room for further investigation in this direction, but even as the matter stands, it seems quite unnecessary to use alloys for the purpose of obtaining high specific resistance.

Quite early in the history of this investigation it was observed that during the heating and cooling of certain resistances, for the purpose of artificial ageing, the resistance changes were not as great as the temperature changes seemed to warrant, and in one noteworthy case the resistance change seemed to be in the wrong direction. Accordingly, the temperature coefficient of this particular film was carefully determined.

This film was deposited April 4, 1898. During the preliminary treatment for bringing it to a condition of stability, its resistance was measured quite frequently. The measurements were made at temperatures differing by a few degrees, and, even during the first few days, while the changes in resistance were quite large, there was at least an indication that the temperature coefficient was probably negative.

On April 21st, the temperature of the film was reduced 19 degrees, and the reduced temperature was kept constant for several hours. This fall of temperature was accompanied by an *increase* of resistance amounting to a little more than 6 ohms, the total resistance of the film being a little less than 2,300, though it had not yet reached its final value. When the temperature of the film was raised to its former value, the resistance *fell* about 4 ohms. The discrepancy between the 6 ohms rise and the 4 ohms fall was due to the fact that the process of artificial ageing was not yet finished, but there was no longer any room to doubt that the temperature coefficient of this film was negative.

[1] Methods of determining approximate thickness will be discussed later.

On April 27th, when the resistance had become more nearly constant, this film was provided with platinum terminal wires, and sealed into a glass tube from which the air was afterwards exhausted to about .001 of an atmosphere, the tube being then hermetically sealed.

Its record on the last three days of the month was as follows :

Date.	Temperature.	Resistance.
Apr. 28, 1898	23.2 degrees.	2284.1 ohms.
" 29 "	2.0 "	2290.5 "
" 30 "	23.1 "	2284.2 "

The temperature coefficient calculated from these results is — 0.00013.

Even at the date of these measurements, this film was not *perfectly* seasoned, but the subsequent changes in resistance were very slight, and after October 1, 1898, no changes whatever could be detected except such as were in exact harmony with the above named temperature coefficient.

In November, 1898, Mr. F. B. Fawcett's very interesting article "On Standard High Resistances" appeared.[1] In this article Mr. Fawcett points out the early rapid decrease in the resistance of a film and the importance of artificial ageing. He also indicates a method of standardizing the resistances and a method of artificial ageing; but in determining the thickness of the films, he assumes that the specific resistance is the same for all films.

The Electrical Contacts.

In these experiments for a considerable length of time the contacts between the films and their terminal wires were an unfailing source of annoyance. Clamps were used at first, but they proved to be untrustworthy. A piece of tin foil or silver foil may be clamped to a *thick* film and the contact may be as good as any clamp contact, which is not saying very much. Of course bright metal plates may be very successfully clamped together for temporary connections, but even the best of clamp connections can hardly be considered first class permanent contacts on standard resistances. Furthermore if a resistance having clamped contacts be boiled in oil

[1] Phil. Mag., 5, Vol. 46, pp. 500–503.

or paraffin for a number of hours, as in the process of artificial ageing, there is a strong probability that the insulating material will get into the joints, especially if the coefficient of expansion of the clamp is greater than that of either of the materials held together.

Aside from all this, when we consider making contacts with a *thin* film, there is an additional difficulty. These films are rather delicate and will not endure the rough usage to which *thick* films, wires and metal plates may be subjected. If the slightest crack be produced in the film, by the pressure of the clamp, the crack will expand and contract under the influence of temperature changes, and in this way a variable resistance will be introduced into the circuit. It was for these reasons that a number of attempts were made, several of which resulted in perfectly satisfactory methods of making electrical contacts with even the thinnest of the films.

The first attempt, which was not altogether successful, is represented in figure 6. (*AA*) are strips of tin foil or platinum foil fastened to the glass with shellac varnish and thoroughly baked. The film (*B*) is deposited afterwards over the entire surface of glass and foil, and if thick enough, the continuity between the film on the glass and the film on the foil is perfect. If, however, the film is thin, there is lack of continuity at the edge of the foil. The method may be used even for thin films by covering the edge of the foil with gold leaf before the film is deposited. This makes a joint which is electrically good, but poor mechanically.

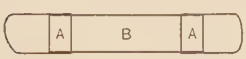

Fig. 6.

The second method is satisfactory in every respect and is applicable to films of any thickness. This method is represented in figure 7. In this case the film is deposited first, and over the entire surface of the glass. The receiver is then opened and the portion (*B*) of the film is covered. The receiver is again closed and exhausted and the deposition of metal is simply continued until the portions (*AA*) are very thick. We then have a continuous film, as thin as we please, for a high resistance, but with *ends* as thick as we please for making connections. The fine copper wires (*CC*) are then wound on and permanently secured by electrolytic deposition of copper on them.

Fig. 7.

The resulting contact leaves absolutely nothing to be desired, but the process is rather tedious. A *thin* film may be produced in a few minutes, after the receiver is exhausted, but these *thick ends* require hours. It was on this account that a third method was devised. Figure 7 represents this method as well as the preceding one. In this case, the ends of the glass plates are first immersed in a silvering solution, and thick films of silver (*AA*) are deposited upon them by any of the well-known methods. As the plate stands in the silvering bath the portion which is below the plane of the surface of the bath becomes heavily coated; but there is a small area just above this plane, which receives silver from only the small amount of liquid which rises above the plane of the surface of the bath by capillary action. For this reason, the film, however thick it may be, always terminates in a very thin edge so that the film (*B*), which is afterwards deposited is perfectly continuous over the entire surface of the glass and silver. The copper wires (*CC*) are secured in this case in the same way as in the preceding case. If the silvering of the ends had to be done one piece at a time, this method would have very little advantage over the preceding one, but, as a large number of plates may be placed in the silvering bath at the same time, the amount of time spent in silvering the ends of the plates is very small.

Fig. 8.

The finished film, as it appears in figure 8, may be introduced into a Wheatstone bridge circuit, or into any other electric circuit for which it is suitable, just as if it were a coil of wire. It has, however, the advantages of being non-inductive and practically without capacity.

(To be continued.)

ELECTRICAL RESISTANCE OF THIN FILMS DEPOSITED BY KATHODE DISCHARGE. II.[1]

By A. C. Longden.

The Electrical Measurements.

THE apparatus used in making the tests to which these resistances have been subjected was such as to afford results of the highest attainable accuracy; and in all cases where accuracy was considered important no painstaking effort has been spared in securing it.

The Wheatstone bridge and rheostat used in the Ryerson Laboratory was one of Queen's, of the kind known as "Set No. 1," No. 80. The rheostat consists of five sets of coils aggregating 11,111 ohms, and guaranteed by the manufacturers accurate to $\frac{1}{50}$ per cent. The bridge is provided with five pairs of reversible bridge coils ranging from a pair of units to a pair of 10,000 ohm coils. These are guaranteed accurate to $\frac{1}{100}$ per cent. The temperature of the coils was determined to within one hundredth of a degree by means of an electrical thermometer placed inside of the box.

Resistances beyond the range of this bridge were measured by the direct deflection method. In applying this method a new form of water battery[2] devised and constructed for this work was found useful, convenient, and comparatively inexpensive. In the construction of this battery, instead of using a copper plate and a zinc plate, two copper plates are used, one of which is amalgamated with mercury containing a little zinc. This plate presents a zinc surface to the water and is therefore equivalent to a zinc plate in the cell, but it does not dissolve in the cell, nor become brittle and break off at the surface of the water as an all zinc plate does. The resistance of this cell may be varied by varying its size, or, within certain

[1] Continued from page 55.

[2] Electrical World, Vol. 31, p. 681.

limits, by the introduction into the water of a *small* quantity ($\frac{1}{10}$ of 1 per cent.) of sulphuric acid. If the cell is properly constructed and sealed it requires no attention whatever for many months at a time, and its electro-motive force is practically constant as long as it is not overworked. Of course it will polarize quite rapidly if used on anything but very high resistance circuits. It is not intended to furnish much current.

In the work done at Columbia University, for measuring resistances of more than a few thousand ohms it was found convenient to use a bridge of the slide-wire type in which a potentiometer of 100,000 ohms forms the two variable resistances. The third resistance was the one under test, while the fourth was a standard of 10,000, 100,000 or a 1,000,000 ohms. The rest of the set consisted of a sensitive Thomson galvanometer and a battery of from one to one hundred dry cells.

The potentiometer used was designed at Columbia University by the late Mr. Holbrook Cushman, and was constructed for the university by a mechanician employed for the purpose. The coils were standardized and adjusted at the University by Mr. H. C. Parker and his assistants. A fuller description of the instrument is given in Mr. Parker's admirable work on Electrical Measurements.

The 10,000 and 100,000 ohm standards were made by Elliott Bros. of London. The 1,000,000 ohm standard was one of the platinum film resistances under discussion, but its resistance was frequently measured and it was found to be perfectly trustworthy.

With this apparatus a resistance as high as 20 megohms may be measured to within one part in 10,000.

In making the measurements for determining temperature coefficients, the standards of comparison were kept in the electrical testing room in the Fayerweather Laboratory. The resistances under test were first measured in that room at the same temperature as the standards, and again after being removed to an underground constant temperature room, located just outside of the main wall of the building, and entered from the sub-basement. One arm of the bridge in the testing room was connected with a mercury commutator in the underground constant temperature room by a well insulated, heavy copper wire circuit of small but known resistance.

For all high resistance work this circuit is negligible. If the resistance to be measured is small enough to make it at all important, the resistance of the line is deducted. The temperature changes in the line itself are very slight, but of course the method is not used for measuring resistances so small that temperature changes in the line itself would produce appreciable errors in the results.

The temperature of the testing room is ordinarily about 20° C., and does not usually vary more than a degree during the course of a day. The temperature of the underground room is generally about 10° or 11° and changes very slowly. These temperatures were measured by means of well seasoned thermometers which have been carefully standardized by comparison with a thermometer accompanied by a Reichsanstalt certificate dated May 7, 1898.

This method of measuring resistances at different temperatures proved to be at once convenient and, what is much more important, reliable. Convenient, because no special precautions were necessary in order to maintain constant temperatures, and reliable because there could be no doubt about the temperature of a film or coil which had remained undisturbed in a constant temperature room for two or three days.

In measuring the temperature coefficients of film resistances, it was soon noted that all of the very thin films had negative temperature coefficients, while all of the thick ones had positive temperature coefficients, and that for a certain range of thicknesses the temperature coefficients were close approximations to zero. It was also noted that, unfortunately, some other factor besides thickness enters into the condition which produces zero temperature coefficients. This other factor may be, and probably is, density; for this is obviously the most variable property of the films. When it becomes possible to hold all the conditions under which the films are deposited in perfect control, it will, doubtless, be possible to produce zero temperature coefficients or temperature coefficients of any desired value by simply producing films of certain thicknesses. Even under present conditions the range of thicknesses for negligible temperature coefficients is not small.

Before proceeding further with this part of the subject it may be well to state that for convenience a standard length and breadth

were adopted for all films, so that, as the thickness was the only varying dimension, its relation to temperature coefficients might the more easily be discovered. Therefore, wherever in this article films are in any way compared, it may be assumed that they are films of equal length and breadth. The adopted total length of the glass plate is 7 cm., but as a centimeter at each end is covered with a *thick* film of negligible resistance for making the electrical connections, the length of the *thin* resistance film is 5 cm. The breadth is in all cases 15 mm.

A platinum film of the above dimensions thick enough to have a resistance of only about 400 ohms, has a positive temperature coefficient equal to 0.0003. The largest negative temperature coefficient measured was — 0.005. This was for a film so thin as to have a resistance of about 18 megohms. If the curve connecting temperature coefficients with thickness, were a straight line, zero temperature coefficients would occur at about one megohm, for films of these dimensions, as seen by the position of the dotted line in Figure 9. As a matter of fact, however, zero or negligible tem-

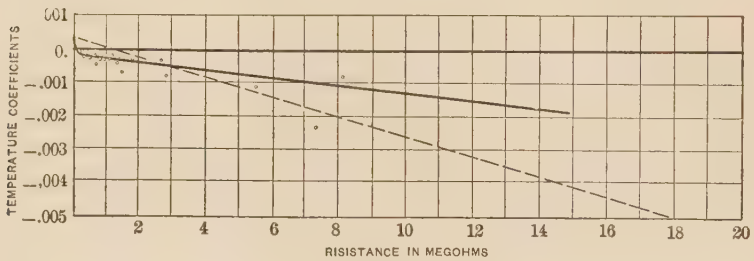

Fig. 9.

perature coefficients frequently occur in resistances of less than 5000 ohms, and they occur all along from that point to somewhere in the neighborhood of 100,000 ohms. It must also be remembered that the very large negative coefficient mentioned above is an extreme case. The large number of results indicated by the points between the axis of ordinates and the two-megohm line in Figure 9 indicates that for films of a certain density the real position of the curve is probably not far from that represented in the figure. Fortunately the range of low temperature coefficients, from a few thousand ohms up to about a megohm, is an exceedingly useful

one. It could hardly have happened to occur in a more desirable place.

Adjusting and Standardizing Film Resistances.

It is important to consider in connection with the question of temperature coefficients, a method of adjusting these resistances to a particular value. The method referred to is substantially the same as the one described by Mr. Fawcett. It was also used in this investigation as early as June 2, 1898. It consists of simply cutting the film into sections, as in Fig. 10, so as to increase the length and diminish the breadth of the conductor. In this way the resistance of a film may easily be increased ten fold or even much more than that, if necessary.

Fig. 10.

Of course a resistance may in this way be adjusted to any desired value, provided the final value is to be *higher* than the original value; but the importance of the method in connection with the question of temperature coefficients is in the fact that a film *thin* enough to have a resistance of several megohms is quite likely to have a rather large negative temperature coefficient (see Fig. 9), while a film of something less than 100,000 ohms resistance with a zero or negligible temperature coefficient may, by means of the method here described, have its resistance increased to the higher value without altering its temperature coefficient.

For making very high resistances with zero temperature coefficients it is advisable to use wider plates, so that the current may be made to traverse the length of the plate a greater number of times without making the conductor dangerously narrow.

Fig. 11.

The same result may be accomplished by bending a small glass tube or rod into the form shown in Fig. 11 and depositing upon it a film of such thickness as to have a zero or neglible temperature coefficient. In this case, however, the final adjustment to a required value is not quite so easy.

Aging and Protecting the Films.

The change in resistance which a film undergoes, quite rapidly at first, and less rapidly later, makes the "artificial aging," or "sea-

soning" process one of great importance. There are, however, no difficulties connected with it. It is the same process for films as for wire resistances. The films may be heated and cooled in the air, or they may be boiled in oil or in melted paraffin. In any case the process is rather a tedious one and should not be considered at an end until sometime after the point has been reached where no further change is noticeable. Otherwise the resistance will continue to undergo slight changes for a considerable length of time. The following table exhibits some of the results of perfect and imperfect artificial aging:

		Resistance in Ohms.			
Class A.	1	2265.8	2265.7	2265.8	2265.8
		37586.	37585.	37588.	37586.
Class B.	3	384.90	383.72	383.16	382.92
	4	9999.5	9992.5	9990.3	9989.4
	5	15722.	15697.	15685.	15681.
	6	23335.	23680.	23765.	23774.
	7	165200.	167680.	167880.	167930.
Class C.	8	84167.	83710.	83431.	83178.
	9	656030.	653600.	651620.	650110.
	10	4690000.	5008000.	5070000.	5080000.

The values given in the successive columns are for measurements about a month apart, and either made at the same temperature or reduced to the same temperature; the temperature coefficients of all the films having been carefully determined.

The films in class (A) were thoroughly seasoned; while those in class (B) were less perfectly seasoned and those in class (C) were very poorly seasoned. It will be observed that in class (C) the variations amount to as much as two or three tenths of 1 per cent. even during the third month. In class (B) the corresponding variations are only a few hundredths of 1 per cent.; while in class (A) no change greater than could be attributed to errors of observation was detected during the entire duration of the test.

In subjecting a number of films to the process of artificial aging, a rather important relation between this process and temperature coefficients was observed. By keeping the films connected with

the Wheatstone bridge during the aging process, it was seen that the resistances did not continue to change in the *same direction* during the entire process. It was observed, first, that if the rapid change of resistance which occurs when the film is first placed in a hot bath is an *increase*, it will soon reach a maximum and then gradually *decrease* for a number of hours; second, that if the first rapid change is a *decrease*, the later and more gradual change will be an *increase;* and third, that if the resistance does not change at first it will not change at all. Now a film of the first kind always has a positive temperature coefficient, while one of the second kind always has a negative temperature coefficient. Of course the temperature coefficient of the third kind is zero.

The sign, and roughly the value of the temperature coefficient of a film resistance may be determined by holding a glowing incandescent lamp within about an inch of the film, while the latter forms one arm of a balanced Wheatstone bridge. If the resistance does not change at all the temperature coefficient is zero and the film does not need much artificial aging. Briefly stated, the changes in resistance which occur during the process of artificial aging, and the length of time required to bring the resistance to a permanent value, are proportional to the magnitude of the temperature coefficient. Therefore a low temperature coefficient is important, not only for its own sake, but also as a means to an end. Films having low temperature coefficients are very easily seasoned and extremely reliable after seasoning.

It is probably true that in films there are not as many causes at work to create a necessity for artificial aging as in the case of wires.

It has recently been found by C. de Szily[1] that if a wire be subjected to *torsion* its electrical resistance increases, and that if the torsion is maintained the resistance very slowly diminishes with time. Also that a wire, which, after dextral torsion, has been relieved and then twisted by sinistral torsion to the zero position, diminishes in resistance more quickly that when the twist is maintained. Also that when a wire has been twisted beyond its elastic limit, and has been allowed to untwist itself, subsequent changes of

[1] Comptes Rendus, Vol. 128, pp. 927–930.

resistance for torsion are less than those which occur during the first twist. It is probable that stretching, bending and even winding upon a spool all produce a similar condition in wires.

After the artificial aging process is at an end it is important that the films be protected from the air in order that no new conditions may arise to produce changes in resistance. They may be enclosed in glass tubes from which the air is exhausted, they may be simply imbedded in paraffin, or they may be coated with varnish prepared by dissolving India-rubber in carbon bisulphide.

Thickness of Films.

In consideration of the relation which evidently exists between thickness of films and temperature coefficients, it seems desirable to be able to measure the thickness of the films.

It is to be regretted that no method of making an exact determination of the thickness of the *very thin* films has been discovered. Miss Stone calculated the thickness of her films from their weight and area, assuming that the density was the same as that of silver in its ordinary condition. However correct or incorrect this method may have been for silver films deposited from aqueous solutions, it certainly would not be very useful in determining the thickness of films of such varying compactness as those deposited by kathode discharge. Furthermore, many of the films considered in this research are entirely too thin to produce any impression whatever upon the most delicate balance; so that both density and weight are unknown quantities. Even if an exact determination of weight could be made, it would be of doubtful value, because of the varying and always indefinite amount of air and other gases absorbed by the film and weighed with it. The property of absorbing and occluding gases does not belong to platinum alone. It is possessed in some degree by a large number of metals.

For this and other reasons it was deemed desirable to attempt to determine the weight of a few films by the methods used in quantitative chemical analysis. Silver was the metal chosen for these experiments, because of the very delicate and exact existing method for its quantitative determination. After the films were deposited, they were converted into silver nitrate and then subjected to the

volumetric process known as Gay-Lussac's method. The quantity of silver in these films was so small that although the method of analysis used was the one which Fresenius describes as "The most exact of all known volumetric processes," yet it was not possible in any case to make an exact determination of the amount of silver in a *transparent* film, and if the films were really *thin* it was not even possible to *detect* any silver in the solution. These facts are mentioned as forcible illustrations of the exceeding thinness of the films.

The assumption upon which Mr. Fawcett bases his method of calculating thickness is certainly unwarranted; for in very thin films, the ratio of the measured resistance to the calculated resistance is unquestionably very much higher than it is in thicker films.

Professor Michelson's interferometer furnishes a direct method of measuring the thickness of comparatively *thick* films, but that is not the important part of the problem; for even a thick film, in the sense in which the terms thick and thin are here used, is only one or two tenths of a wave length thick. However, a few comparative experiments were made upon thick films, determining the thickness by means of the interferometer and also from weight and area. In some cases the results were fairly concordant, indicating that in these cases the density was about normal.

A silver film which was just transparent enough to reveal the outline of a luminous gas jet was used in making one of these comparisons. A portion of the film was removed from the glass and the optical difference of path between the surface of the glass and the front surface of the film, was measured by means of the interferometer. The displacement of the interference fringes due to this difference of path was about .3 of a fringe. (Sodium light.) The thickness of the film is therefore about 0.00009 mm. The thickness of the same film, calculated from its weight, 0.0008 g., and area, 7.38 square centimeters, assuming a density of 10.55, was 0.00010 mm. A platinum film somewhat more transparent was found by the interferometer method to have a thickness of 0.00006 mm., while its thickness, calculated from its weight and area was 0.000063 mm. This, however, does not prove that the density of thin films is the same as that of thick ones or even that the density is the same for all films of the same thickness.

It must be remembered that both of the films just considered were *thick* films. The utter uselessness of attempting to weigh very *thin* films is illustrated by the fact that a platinum film 15 mm. wide and 5 cm. long, weighing only .0.00025 g. has a resistance of only about 2000 ohms. What would be the weight of a film thin enough to have a resistance of several megohms?

Photometric methods are of some service, for they at least give an indication of the amount of metal in a film which is too thin to be weighed, but the results obtained by this method do not agree to within 10 per cent.

There is yet one method of estimating thickness to be considered.

It seems reasonable to suppose that the rate of deposition must be uniform under uniform conditions, and that therefore the thicknesses of films ought to be directly proportional to the times required for their deposition; provided only that none of the conditions are allowed to change during the process. The electro-motive force, current and distance are under perfect control. The frequency of the Wehnelt interrupter is not very difficult to control if the temperature is kept constant by means of a cold water circulation. Even the vacuum may be kept within reasonable limits if very great care is exercised during the first part of the process, while the occluded gases are being expelled. It is therefore believed that the time element in the deposition of a film may be made the most reliable basis for estimating thickness; and it is this element that has been trusted more than any other in the estimates of thickness which have been made during the progress of this research.

CHOICE OF MATERIALS.

In the choice of a metal for the production of film resistances, permanence has been the chief consideration, and platinum, all things considered, is believed to be the most suitable metal. Gold is doubtless just as permanent as platinum as far as its ability to resist chemical action is concerned; but its molecular condition does not settle down to a permanent value as that of platinum does. H. L. Callendar in his work "On a Practical Thermometric Standard"[1] condemns gold as a material on the ground that there is a slow but

[1] Phil. Mag., S. 5, Vol. 48, pp. 519-547.

constant change of zero in a gold thermometer. This of course, means a slow but constant change of electrical resistance at a certain temperature. It is for this reason that gold is not a suitable metal for resistance standards.

A number of other metals have been experimented upon, but none of them seemed to possess any advantage over platinum.

Summary of Results.

The conclusions drawn from this investigation, briefly stated, are as follows :

(1) The process of depositing metals by kathode discharge as illustrated by figures 3, 4 and 5, is probably simple *distillation*, in which the vaporization of the kathode is largely due to its electrification.

(2) The temperature coefficients of the very thin films are negative, and for films within a certain range of thicknesses, the temperature coefficients are approximately zero.

(3) The necessity of artificial aging is proportional to the magnitude of the temperature coefficient.

It may be said in general that the method herein described is capable of producing standard electrical resistances of a very high degree of precision and of any desired value, from a few ohms up to several megohms ; that these resistances may be made of pure metals—simple elementary substances—and that they are therefore free from the possibility of decomposition changes ; that the metals may be those least likely to enter into chemical combination with other elements ; and that in addition to these valued qualities as pure metals, they possess the only desirable qualities of alloys, namely high specific resistance and low temperature coefficients.

In closing this dissertation I wish to express my sincere thanks to Professors Rood and Hallock, of Columbia University, for their kindly interest in my work and for the many helpful suggestions which they have given me. Also to Professors Michelson and Stratton, of the University of Chicago, for valuable assistance during the early part of the investigation.

Fayerweather Physical Laboratory,
Columbia University, March 31, 1900.

VOLUME XI NUMBER 2

THE PHYSICAL REVIEW

A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED BY

EDWARD L. NICHOLS

ERNEST MERRITT, and FREDERICK BEDELL

LVI

AUGUST 1900

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BY THE MACMILLAN COMPANY

LANCASTER, PA., AND NEW YORK

LONDON: MACMILLAN AND CO., LTD

BERLIN: MAYER AND MUELLER